

# Calculation of Rovibrational Energy Levels of Diatomic Molecules by Dunham Method with Potential Obtained from *Ab Initio* Calculations

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**ABSTRACT:** A numerical algorithm of the Dunham method for the solution of the rovibrational Schrödinger equation is proposed. It uses a new quasi-Hermitian method of constructing the optimal approximate polynomial for the tabularly defined potential curve of a diatomic molecule obtained from an *ab initio* calculation. In this method the optimal polynomial approximates the potential curve and its derivatives, but it uses only information about the potential curve for its construction. This property of the new method arises from analysis of a spectral representation of the optimal polynomial to determine how well it approximates the potential curve and its derivatives. Appropriate derivatives of the potential curve, needed in the Dunham method, are calculated by recurrence relations. Comparison with the finite-difference method shows that the precision of both methods is similar, while the Dunham method is hundreds of times faster. © 1998 John Wiley & Sons, Inc. *J Comput Chem* **19**: 94–101, 1998

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## Introduction

It is well known<sup>1</sup> that the rovibrational energy levels of diatomic molecules can be described by the formula

$$G(\nu, J) = \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} Y_{kl} \left( \nu + \frac{1}{2} \right)^k [J(J+1)]^l, \quad (1)$$

where  $\nu$  is the vibrational and  $J$  is the rotational quantum number. The same energy levels can be found from the solution of the Schrödinger equation,

$$\frac{d^2\Psi}{dR^2} + \left( E - U(R) - \frac{J(J+1) + \Lambda^2}{R^2} \right) \Psi = 0, \quad (2)$$

where  $U(R)$  is a potential in which the nuclei of the molecule are moving,  $J$  is the rotational quantum number, and  $\Lambda$  is the projection of the electronic moment on the axis of the molecule.<sup>1</sup> Dunham solved this equation by a quasiclassical method<sup>2</sup> for the  $\Sigma$  state ( $\Lambda = 0$ ) by assuming that the  $U(R)$  potential is an analytical function described by the series

$$U(R) = a_0 \left( \frac{R - R_e}{R_e} \right)^2 \left[ 1 + \sum_{n=1}^{\infty} a_n \left( \frac{R - R_e}{R_e} \right)^n \right], \quad (3)$$

where  $R_e$  is the coordinate of the minimum in  $U(R)$ . As a result he was able to express the  $Y_{kl}$  coefficients in terms of the  $a_n$  parameters.<sup>3</sup> This made it possible to determine the  $Y_{kl}$  coefficients without a direct solution of the Schrödinger equation. A similar approach was used in refs. 4–7 to obtain the  $Y_{kl}$  coefficients for new values of  $k$  and  $l$  and for known values but in a higher order of perturbation theory (PT). The largest number of formulae for  $Y_{kl}$ , up to  $k = 7$  and  $l = 9$ , was obtained in refs. 8 and 9 by use of a special system of analytical transformations on a computer.

Note that the representation of the potential curves of diatomic molecules by series (3) has a serious disadvantage due to the limited radius of convergence  $0 < R < 2R_e$ . Therefore, other formulae with a much larger radius of convergence have been proposed and new formulae for the  $Y_{kl}$  coefficients have been obtained in some cases.<sup>10–20</sup> However, for the energy level calculation in accor-

dance with eq. (1), it is much more important to know as much as possible the number of the  $Y_{kl}$  coefficients. Expressions for the  $Y_{kl}$  coefficients are now known only for restricted values of  $k$  and  $l$ . The largest number of expressions for the  $Y_{kl}$  coefficients is derived for Dunham series (3). Therefore, only this representation of the potential curve shall be considered in the present work.

Analysis of eqs. (1) and (3) shows that three objectives must be reached in order to calculate the energy levels of diatomic molecules by the Dunham method: define the summation limits in eq. (1), approximate the potential curve of a diatomic molecule, and determine the  $Y_{kl}$  coefficients themselves.

The last two problems are closely related. In the Dunham method the calculation of the  $Y_{kl}$  coefficients reduces to the determination of the  $a_n$  parameters of the potential  $U(R)$  in eq. (2). In turn, the problem of finding  $a_n$  leads to a calculation of the derivatives of the required orders at the minimum point, because series (2) is a Taylor expansion of  $U(R)$  about the point  $R_e$ . Thus, we arrive at

$$a_n = \frac{R_e}{2} \left( \frac{d^2 U(R)}{dR^2} \right)_e, \\ a_n = \frac{R_e^{n+1}}{a_0(n+2)!} \left( \frac{d^{n+2} U(R)}{dR^{n+2}} \right)_e, \quad (4)$$

where the subscript  $e$  specifies calculation of the derivatives at the minimum point.

In the Dunham method the calculation of the derivatives of the potential curve does not present a problem because it is assumed that the  $U(R)$  potential function belongs to a  $C^\infty(0, +\infty)$  space of functions, which are infinitely differentiable between the limits. In *ab initio* calculations this assumption no longer applies. In this case the potential curve of a diatomic molecule is calculated as a table, that is, for a finite segment with a finite number of significant figures. This method of defining the potential curve means that each segment can only belong to a  $C^M[a, b]$  space of functions continuously differentiable  $M$  times in the segment. The method commonly used to calculate the derivatives of tabulated functions consists of selecting an approximating function and using it to find the minimum point and to calculate the required derivatives. Thus, we can conclude that a method that can be used for approximation of the potential curve must describe the potential curve and its derivatives equally well. The well-known

Hermite approximation type methods cannot be used in this case, because they use both functional values and derivatives. Therefore, a new quasi-Hermite method of approximation of a table-defined potential curve has been developed and implemented in a numerical algorithm of the Dunham method as described below.

It should be noted that several methods have been proposed for the calculation of the  $Y_{kl}$  coefficients with a table-defined  $U(R)$  potential.<sup>21–25</sup> However, each of them only approximates the potential curve and not its derivatives. Therefore, the calculation of the  $Y_{kl}$  coefficients by these methods is possible only for  $k, l \leq 2$  in second-order PT due to numerical instability. In short, these methods cannot be applied to the calculation of energy levels from eq. (1). The proposed numerical algorithm of the Dunham method solves this problem by using a new quasi-Hermitian approximation method.

### Approximation of Tabularly Defined Potential Curve in Dunham Method

Let us consider the approximation of a potential curve by a polynomial. This leads us to the problem of approximating a tabulated function belonging to the  $C^M[a, b]$  space by a function from the  $C^L[c, d]$  space, where  $0 \leq c \leq a$ ,  $b \leq d \leq +\infty$ , and  $L$  is the order of the polynomial. From a practical point of view, the problem thus formulated is indeterminate because the  $C^M[a, b]$  space is not known.

This indeterminacy is related to the problem of optimizing the degree of the approximating polynomial, as discussed previously in refs. 22 and 25. An obvious solution of this problem is to choose  $L = M$  for the  $C^L[c, d]$  subspace. The problem of the optimum order of the approximating polynomial is also related to the numerical stability of the chosen method of constructing the approximating polynomial. Therefore, the algorithm used to determine the optimum approximating polynomial should be capable of establishing the order and coefficients of the polynomial in each particular case.

In this connection let us consider the convergence of the series of  $\{P_n(R)\}$  polynomials to  $U(R)$ . We know that  $\{P_n(R)\}$  converges to  $U(R)$  if

$$\lim_{\substack{n \rightarrow \infty \\ \forall R \in [a, b]}} \|P_n(R) - U(R)\| = 0$$

by the appropriate norm. In actual calculations we cannot construct an infinite polynomial series. Therefore, the optimum polynomial can be defined by the condition

$$\min_{n \in [5, N]} \min_{\substack{\{b_k\}_{k=0}^n \\ i \in [0, N]}} \left\| \sum_{k=0}^n b_k P_k(R_i) - U(R_i) \right\|, \quad (5)$$

where  $\{R_i\}_{i=0}^N$  are the points for which the  $U(R)$  values are given,  $[0, N]$  is the sequence of integers from 0 to  $N$ , and  $[5, N]$  is the same sequence of numbers from 5 to  $N$ . It is assumed that the polynomial is written as a sum of orthogonal polynomials. This does not affect the issue fundamentally, but it allows a more general case to be dealt with. The choice of 5 as the smallest order of the approximating polynomial is due to the fact that  $Y_{20}$  in second-order PT is expressed through the  $a_1$  and  $a_2$  coefficients, and as follows from (4), the parameter  $a_2$  can be determined by starting from a fourth-order polynomial. Furthermore, to give a correct description of the dependence of the  $a_2$  parameter on  $R$ , the order of the approximating polynomial should be increased to least at 5.

In order to use criterion (5), the space in which the approximation will be applied must be defined. Let us consider the  $C^M[a, b]$  space. The norm in this space is defined as follows (see, for example, ref. 26):

$$\|f(R)\|_{C^M} = \max_{R \in [a, b]} |f(R)| + \sum_{k=1}^M \max_{R \in [a, b]} \left| \frac{d^k f(R)}{dR^k} \right|; \quad (6)$$

that is, for the approximation in  $C^M[a, b]$  space we need to know not only the function itself but also  $M$  of its derivatives. However, because the derivatives are not known, norm (6) must be reduced to the norm

$$\|f(R)\|_C = \max_{R \in [a, b]} |f(R)|; \quad (7)$$

that is, we must change the  $C^M[a, b]$  space to the  $C[a, b]$  space. It is also evident that the approximation in  $C[a, b]$  space must be supplemented by a criterion that allows the adequacy of the approximation of the differentials of the potential curve to be calculated. Such a criterion could be formulated from a harmonic analysis of the approximating polynomial. At the same time the problem of approximating the potential curve can be divided into two parts: the approximation itself, and the analysis of the chosen approximating polynomial

with the aim of establishing how precisely it describes the differentials. It is also evident that in addition to an approximation in  $C[a, b]$  space, we can use an approximation of the potential curve in  $L_2[a, b]$  space (in terms of the integration of the squared functions). The norm in this space is

$$\|f(R)\|_{L_2} = \left[ \int_a^b [f(R)]^2 dR \right]^{1/2}. \quad (8)$$

Norm (7) is stronger than norm (8), but because in the Dunham method  $U(R)$  is assumed to be an analytical function, the difference between the approximation in  $C[a, b]$  and in  $L_2[a, b]$  space cannot be very large.

Let us now examine the method of approximation. In  $C[a, b]$  space there are the interpolation<sup>27–33</sup> and the minimax approximation,<sup>34</sup> while in  $L_2[a, b]$  space there is the least squares approximation.<sup>27,35</sup> An analysis of different approximative methods in conjunction with condition (5) shows the superiority of the minimax approximation and the least squares method over the interpolation method due to the property of the interpolation process defined by the Faber and Feier theorems (see, for example, ref. 27).

As pointed out above, the problem of the optimum approximation polynomial is related to the numerical stability of the method of approximation. It is well known in numerical analysis<sup>36</sup> that the stability of the methods of approximation can be significantly improved and hence increase the order of the optimum approximating polynomial by using an orthogonal system of polynomials. The Chebyshev systems of polynomials of the first and the second kind and the Legendre polynomials have been chosen due to their ability to assign different weights to the abscissa points of the approximated function.<sup>27,33</sup>

In addition to increasing the stability of the approximation method, orthogonal polynomials allow us to control the convergence of the differentials of the potential curve toward their limiting values. This control can be realized by monitoring the behavior of the expansion coefficients of the approximating polynomial in a set of orthogonal polynomials. In practice, this means applying a spectral analysis to the resulting polynomial. Three stages can be identified in the search for the optimum order of the approximating polynomial: the order of the resulting polynomial is smaller than, equal to, or greater than the optimum value. The expansion coefficients of the resulting polynomial

in terms of the orthogonal polynomials will behave differently in these three stages.

We now examine the changes in  $b_k^n$  on passing from a polynomial of order  $n$  to a polynomial of order  $n + 1$ . Let the potential curve of the molecule be approximated by a polynomial of order  $n$ , and let  $b_k^n$  be the expansion coefficients of this polynomial in a set of orthogonal polynomials. When the order of the resulting polynomial is lower than the optimum, the behavior of  $b_k^n$  will be regular. This denotes a monotonic decrease in the absolute values of  $b_k^n$  as the order of the orthogonal polynomial increases. When the order of the polynomial exceeds the optimum order, the behavior of the coefficients becomes nonregular. In this case the absolute values of  $b_k^n$  do not decrease monotonically with the increasing order of the orthogonal polynomial. This effect is seen most clearly in the coefficients of the orthogonal polynomials of the highest powers. Such behavior for the coefficients results in a sharp change of the derivatives of the polynomials upon change of the polynomial order and is indicative of poor approximation of the derivatives. However, according to criterion (5), the approximation of the potential curve by the polynomial can be improved by increasing the polynomial order. Therefore, a natural choice for the condition of changing behavior of the expansion coefficients from regular to nonregular (i.e., the criterion for defining the optimum order of the approximating polynomial) is

$$|b_k^n| \geq |b_{k-1}^n|. \quad (9)$$

Condition (9) allows us to identify the polynomial that gives the best approximation to the differentials of the potential curve. By using conditions (5) and (9) we can completely define the optimum polynomial, the polynomial that gives the best approximation to the potential curve and its differentials.

The proposed algorithm for approximation of the potential curve of a diatomic molecule has been examined in the approximation to the potential curve of the  $X^1\Sigma^+$  state of the LiH molecule presented in Table I. The potential curve was calculated by the restricted Hartree–Fock–Roothaan method with the HONDO program.<sup>37</sup> The set of basis functions consists of 8s and 3p Slater orbitals approximated by linear combinations of three Gaussian functions.<sup>38</sup> The equilibrium point was determined by minimizing the total energy of the molecule. Its coordinates were found to be  $R_e = 3.036506$  au. and  $E_{\min} = -7.90227462$  au.

**TABLE I.**  
**Potential Curve for  $X^1\Sigma^+$  Ground State of LiH Molecule.**

$R$ (au)	$U(R)$ (au)
2.50	-7.888196895
2.70	-7.897435270
2.75	-7.898879390
2.80	-7.900034607
2.85	-7.900925442
2.90	-7.901574404
2.95	-7.902002169
3.00	-7.902227738
3.05	-7.902268588
3.10	-7.902140795
3.15	-7.901859153
3.20	-7.901437279
3.25	-7.900887704
3.30	-7.900221965
3.50	-7.896597328

The coefficients of the expansion of the polynomials of order 8, 9, and 10 in the series of Chebyshev polynomials of the second kind obtained by approximating the initial points by least squares are given in Table II. Their root mean square deviations are 0.48D-10, 0.45D-10, and 0.35D-10, respectively; that is, according, to criterion (5), the polynomial of order 10 is the best. However, the results in Table II show that condition (9) is fulfilled by the polynomials of order 8 and 9 but not of order 10. Therefore, the joint use of conditions (5) and (9) to identify the optimum polynomial points for the ninth-order polynomial as the best.

**TABLE II.**  
**Approximation of Potential Curve for  $X^1\Sigma^+$  Ground State of LiH Molecule.**

Polynomial Power RMS	8 0.48-10	9 0.45-10	10 0.35-10
$U_0$	-0.789985 + 1	-0.789985 + 1	-0.789985 + 1
$U_1$	-0.136608 - 2	-0.136608 - 2	-0.136608 - 2
$U_2$	0.241924 - 2	0.241924 - 2	0.241923 - 2
$U_3$	-0.361952 - 3	-0.361954 - 3	-0.361954 - 3
$U_4$	0.378204 - 4	0.378204 - 4	0.378147 - 4
$U_5$	-0.333864 - 5	-0.333876 - 5	-0.333876 - 5
$U_6$	0.295714 - 6	0.295714 - 6	0.295702 - 6
$U_7$	-0.263725 - 7	-0.256042 - 7	-0.256042 - 7
$U_8$	0.151384 - 8	0.151384 - 8	0.541306 - 8
$U_9$		0.490924 - 9	0.490924 - 9
$U_{10}$			0.173367 - 8

The expansion coefficients of the approximating polynomial in a series of the second kind of Chebyshev polynomials of order 8, 9, and 10.

The coordinates of the minimum point determined for this optimal polynomial were found to be  $R_e = 3.036509$  au. and  $E_{\min} = -7.90227482$  au. They do not differ significantly from the coordinates of the minimum point determined by minimizing the energy functional. This shows that a good approximation to the potential curve has been achieved.

**Calculation of  $Y_{kl}$  Coefficients**

It was pointed out above that the calculation of  $Y_{kl}$  coefficients reduces to the calculation of the derivatives of the potential curve at the minimum point. When  $U(R)$  is in the form of a power series of  $R$ , the derivatives can be calculated without difficulty. A more complex situation is met when  $U(R)$  is expressed through a series of orthogonal polynomials. In this case the derivatives can be calculated by recurrence relations. For Chebyshev polynomials of the first kind and for Legendre polynomials the necessary formulae are given by Fletcher.<sup>39</sup> In the case of Chebyshev polynomials of the second kind suitable formulae can be derived. If

$$\frac{dV(R)}{dR} = W(R), \quad V(R) = \sum_{j=1}^N c_j u_j,$$
$$W(R) = \sum_{j=1}^{N-1} d_j u_j,$$

we obtain the following formulae for the  $d_j$  coeffi-

**TABLE III.****The  $Y_{kl}$  Coefficients of Potential Curve for  $X^1\Sigma^+$  Ground State of LiH Molecule.**

$Y_{kl}$	PT Order	Value ( $\text{cm}^{-1}$ )	$Y_{kl}$	PT Order	Value ( $\text{cm}^{-1}$ )
00	6	0.927953	03	8	0.959050 – 07
10	4	1439.468	13	6	–0.102137 – 09
20	6	–21.479	23	8	–0.190507 – 09
30	4	0.250691	04	10	–0.151935 – 10
40	6	–0.683514 – 03	14	8	0.122216 – 12
01	4	7.408901	24	10	–0.137362 – 12
11	6	–0.195763	05	8	0.284253 – 14
21	4	0.197919 – 02	15	10	–0.855685 – 16
31	6	0.741113 – 04	06	10	–0.559801 – 18
02	6	–0.789175 – 03	16	12	–0.150733 – 16
12	8	0.166356 – 04	07	12	–0.139137 – 18
22	6	0.669804 – 06	08	14	–0.248377 – 25
32	8	–0.780219 – 07			

cients:

$$d_{j-1} = \frac{j}{j+2}d_j + 2jc_j, \quad j = 1, \dots, N,$$

$$d_{N+1} = d_N = 0.$$

Recurrence relations can be used to successively calculate the derivatives of different orders needed for the calculation of  $Y_{kl}$  coefficients.

The proposed method of calculating the derivatives was used to obtain the  $Y_{kl}$  coefficients of the ninth-order polynomial given above. It produced the 25  $Y_{kl}$  coefficients listed in Table III. The highest order of the perturbation theory in which the  $Y_{kl}$  coefficients were calculated was 14.

As we know, the smallness parameter in Dunham's method is  $(B_e/\omega_e)^{1/2,2,3}$ . Therefore, the  $Y_{kl}$  coefficients converge very rapidly toward their limiting value as the order of PT used in their calculation is increased. They also decrease rapidly when  $k$  and  $l$  are increased, because new  $Y_{kl}$  coefficients can appear only if the order of the PT is increased. This is confirmed by numerical calculations. Table IV shows the  $Y_{kl}$  coefficients obtained in more than one order of PT for the potential curve of the  $^1\Sigma_g^+$  ground state of the  $\text{N}_2$  molecule taken from ref. 40. The fast convergence of the  $Y_{kl}$  coefficients to their limiting value on increasing the order of the PT shows that the precision of their calculation is acceptable even in the PT order in which they first appear.

**TABLE IV.** **$Y_{kl}$  Coefficients of  $^1\Sigma_g^+$  Ground State of  $\text{N}_2$  Molecule.**

$Y_{kl}$	PT Order	Value ( $\text{cm}^{-1}$ )
00	2	0.313183
	6	0.312923
10	0	2727.565
	4	2727.562
20	2	–10.918413
	6	–10.918116
01	0	2.118281
	4	2.118279
11	2	–0.013790
	6	–0.013793
02	2	–0.511046 – 05
	6	–0.511180 – 05
12	4	0.143020 – 07
	8	0.145007 – 07
03	4	0.743414 – 11
	8	0.743455 – 11
04	6	–0.181064 – 16
	10	–0.181040 – 16

## Calculation of Rovibrational Energy Levels

In the calculation of the rovibrational energy levels of a molecule by eq. (1), we must define the values of  $k$  and  $l$  up to which the summation is to be taken; in other words, we must define the PT

**TABLE V.**  
**Vibrational Energy Levels (cm<sup>-1</sup>) of <sup>1</sup>Σ<sub>g</sub><sup>+</sup> Ground State of N<sub>2</sub> Molecule (J = 0).**

PT Order	0	2	4	6	FD	Ref. 40
G(0)	1363.78	1361.37	1361.37	1361.37	1361.37	1361
G(1)	4091.35	4067.09	4087.13	4067.13	4067.13	4067
G(2)	6818.91	6750.99	6751.15	6751.16	6751.17	6751
G(3)	9546.48	9413.04	9413.51	9413.53	9413.54	9413
G(4)	12274.04	12053.26	12054.27	12054.31	12054.35	12053
G(5)	15001.61	14671.64	14673.50	14673.57	14673.68	14671

FD, energy levels calculated by the finite-difference method.

**TABLE VI.**  
**Vibrational Energy Levels (cm<sup>-1</sup>) of <sup>1</sup>Σ<sub>g</sub><sup>+</sup> Ground State of N<sub>2</sub> Molecule (J = 10).**

PT Order	0	2	4	6, 8, 10, 12, 14	FD
G(0)	1596.79	1593.56	1593.56	1593.56	1593.56
G(1)	4324.36	4297.77	4297.81	4297.81	4297.81
G(2)	7051.92	6980.14	6980.32	6980.33	6980.33
G(3)	9779.49	9640.68	9641.18	9641.19	9641.21
G(4)	12507.05	12279.38	12280.43	12280.47	12280.51
G(5)	15234.62	14896.25	14898.16	14898.23	14898.32

FD, energy levels calculated by the finite-difference method.

order in which eq. (2) must be solved to obtain a solution of the required precision. The rapid decrease of the  $Y_{kl}$  coefficients with increasing  $k$  and  $l$  shows that a very precise solution can be expected, even for a relatively low order of the PT.

We show this by examining the solution of the rovibrational Schrödinger equation with the potential curve of the <sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground state for the N<sub>2</sub> molecule used above. The 25  $Y_{kl}$  coefficients were calculated by using a ninth-order optimal approximating polynomial. The highest PT order used in the calculation of the vibrational coefficients was 6 and for the rovibrational coefficients was 14. The rovibrational energy levels of the N<sub>2</sub> molecule calculated in different PT orders for the rotational quantum numbers  $J = 0$  and  $J = 10$  are shown in Tables V and VI. For comparison these tables also show the energies of the rovibrational levels obtained by solving eq. (2) by the second-order finite-difference method with the same potential. The numerical solution was obtained by a three-point Richardson extrapolation. The solutions obtained by using 900, 1000, and 1100 points were used as the extrapolation points. The CPU time needed for solution of eq. (2) by the finite difference method was hundreds of times greater than those needed for the Dunham method. Table V also presents the vibrational energy levels calcu-

lated in ref. 40 with the same potential curve. The results obtained show that the energies of the rovibrational levels, as expected, converge rapidly to their limiting value as the order of the PT used in their calculation is increased. For the rotational quantum number  $J = 10$ , the energies of the rovibrational levels reach their limit in the sixth order of PT and stay constant beyond this order. The chosen approximating polynomial did not allow the energies of the vibrational states to be calculated above the sixth order of PT. However, we may suggest by analogy that the energies of the vibrational states also reach their limiting values in the sixth PT order. The rovibrational energy levels calculated by Dunham's method are satisfactorily consistent with those obtained by the finite difference method. It follows that the precision of the quantities obtained by solving eq. (2) by Dunham's quasiclassical method is comparable with the precision of the numerical solution.

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